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CORROSION EMBRITTLEMENT OF DURALUMIN

I. PRACTICAL ASPECTS OF THE PROBLEM

By Henry S. Rawdon Bureau of Standards

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I. PRACTICAL ASPECTS OF THE PROBLEM.

By Henry S. Rawdon.

Since aircraft design is trending toward all-metal construction, the strong heat-treatable light aluminum alloy, duralumin,* is finding increasing application. In airplanes, for example, it is used in sheet form, for wing and fuselage coverings, for floats; in tubes, plates and special sections for wing and fuselage structures, as well as in very much thicker sections, for propellers. In lighter-than-air aircraft, practically the entire framework is constructed out of sheet duralumin.

Doubt has been expressed at times concerning the reliability and permanence of these materials. The very extensive and
successful use of the light aluminum alloys for aircraft, however, has served in large measure to refute such imputations. Such
an answer is not entirely satisfactory, however, when it is considered that in the early days of the aircraft industry, especially during the war conditions, much of the aircraft served its
purpose and became obsolete before any serious impairment of the
properties of the material had occurred or at least been detected.

^{*}In this and succeeding reports of the series, the term "duralumin" is used as referring to the class of heat-treatable alloys containing Cu, Mg, Mn, and Si and not to the product of any particular manufacturer.

At the present time, however, conditions are somewhat different. With the greatly increased life, largely as a result of the greatly improved methods of design, that may rightly be expected of modern aircraft, the question of the permanence of the material used in the construction of such aircraft becomes one of increasing importance.

Duralumin does not rust nor does it corrode rapidly in the air, in the ordinary sense of the word. After the initial dulling of the bright surface by brief exposure to the weather, it retains its appearance for years without much change. A comparison of the appearance of weathered duralumin with that of steel which has been subjected to the same corrosive conditions is of particular interest since the behavior of iron and steel serves commonly as a measure of the comparative permanence of metals exposed under atmospheric conditions. Figure 1 shows the appearance of the end of a duralumin girder of the same general type as is used in the construction of airships, the steel end plates having been added in this case for test purposes. The surface condition shown in Figure 1 resulted from three years' exposure on the roof of one of the Bureau of Standards buildings.

The pronounced rusting of the steel, with consequent loss of section, is evident. Ordinarily, however, no doubt would be expressed concerning the condition of the duralumin on the basis of its appearance. Most duralumin under most conditions of use retains for years its initial strength and ductility almost un-

impaired. This is not always true, however. Some duralumin, under some conditions of use, becomes seriously impaired in its properties although it may show no greater evidence of it on the surface than is shown by the duralumin parts in Figure 1.

Corrosion of the Ordinary Type.

Aluminum and the aluminum-rich alloys are readily attacked by a number of strong corrosive reagents, both acid and alkaline. Hydrofluoric acid is a good example of the former and sodium hydroxide of the latter. Specimens of duralumin, when immersed in either of these solutions are vigorously attacked as is evidenced by the copious evolution of gas bubbles. The surface of the metal, as the corrosion proceeds, takes on a matt appearance (beneath the dark film of corrosion products) as a result of the slight roughening (pitting) that occurs. The maximum tensile load which a specimen can carry, after corrosion, is, of course, less than before corrosion, the reduction being proportional to the change in the cross-sectional dimensions of the The tensile properties of the corroded material, as referred to the new cross section of the specimen, however, are only slightly changed, if at all, even if the corrosive attack is a prolonged one, as is shown by the results in Table I. It will be especially noted that the ductility is not affected. respect the effect of corrosion on duralumin is similar to the effect on iron and steel and on many nonferrous metals and alloys. A metallographic examination of the underlying uncorroded metal would show that the metal had not been changed from its initial condition, that is, the corrosive attack consisted in the removal of metal from the <u>surface</u> without penetrating to any appreciable depth into the body of the specimen.

A corrosive attack of this general nature is of more serious consequence in those cases in which the metal is in contact
for a good deal of the time with the liquid corrodent. It is
especially serious in crevices which serve to hold the liquid,
as may sometimes be the case in welded articles. An attack of
this kind is not ordinarily very serious in atmospheric service
unless a good deal of moisture, especially sea spray, is encountered.

TABLE I.

Effect of corrosion on the tensile properties of 14-gauge sheet duralumin, heat-treated by quenching in hot water after being heated 15 minutes in a fused nitrate bath, 500-510°C. The tension specimens after machining were corroded as indicated. (See Table I of the next report of this series for composition.)

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Corrosive treatment	Tensile pr *Ult.Ten.Str.	operties Elong.(2")	Remarks
None	lb./in.2 {61,700 {61,500	per cent 20.0 21.0	
Immersed 5 min. in 10 per cent HF	{61,700 {61,300	19.5 20.5	
Immersed ½ hour in 10 per cent HF (thickness reduced from .064 to .054 inch).	62,000	19.0	Broke outside cen- tral 2-inch gauge-length
	60,800	19.0	Broke outside cen- tral 2-inch gauge length
5 min. in 10 per cent NaOH solution	{59,600 {59,400	18.5) 20.0}	Broke through gauge mark
l hour in 10 per cent NaOH solution (thick ness reduced from .064 to .034 inch)	- {62,100 59,200	19.0 18.5	Broke through gauge mark Broke through gauge mark

^{*}Referred to true section.

Intercrystalline Corrosion.

Some sheet duralumin, under some conditions of use, does not maintain its original properties without impairment. striking, and perhaps somewhat exceptional, example is that of the sheet-duralumin wing covering of a J-L airplane, originally strong enough to permit one to walk upon it, which became so brittle after two years' exposure (following its use in service) on the seashore at the Naval Air Station at Hampton Roads, Va., that the finger could be thrust through the sheet metal. type of corrosion, by which the mechanical properties of sheet duralumin may be very greatly affected, appears to be quite different from the more familiar one. The general effect upon the properties consists in a pronounced lowering of the ductility of the material accompanied by a somewhat smaller decrease in tensile strength, in contrast with the effect of the type of corrosion previously discussed. This is illustrated by Figure 2, a and b, which shows the appearance of a tested tension specimen of sheet duralumin which during atmospheric exposure (8 months) became very weak and brittle. The "multiple cracks" shown by the tested bar are characteristic of this embrittled condition and give to the material an apparent elongation which is greater than really exists. Figure 2c illustrates how seriously the bending properties of the material may be affected by corrosion of this kind. The bend test is a simple and satisfactory means of showing the presence of advanced embrittlement

of sheet material as a result of this type of corrosion.

A metallographic examination of sheet duralumin corroded in a manner so as to cause this pronounced change in properties, shows that a pronounced structural change has occurred which accounts for the change in tensile properties. This is depicted in Figure 2,d - which shows a complete cross section of the sheet of Figure 1,c, which had been very severely embrittled by corro-Usually the attack is not so pronounced as this but is confined to the material immediately adjacent to the surface as is shown in Figure 2,e. The characteristic feature of this type of corrosive attack is the fact that it penetrates into the metal and is not merely a surface attack as is the foregoing type. The corrosion is confined almost entirely to the grain boundaries and in penetrating into the metal, the path followed is an intercrystalline one. For this reason, this type of corrosive attack is termed "intercrystalline corrosion." It is with the deterioration of duralumin by this form of corrosion that the investigation discussed in the following reports has been largely concerned.

Sheet duralumin which has been subjected to intercrystalline attack would, on the basis of our general knowledge of endurance testing, be expected to show a greatly lowered endurance limit or resistance to "fatigue stresses." This expectation is borne out by the data given in Figure 3, which shows the results obtained for specimens of embrittled sheet duralumin together with

the results of "normal" sheet material of approximately the same thickness.* Any abrupt change in the cross-sectional area of a specimen subjected to vibratory or "fatigue stresses," particularly when in the form of a notch, builds up locally the maximum fiber stresses far above the computed average for the whole specimen. The narrower and deeper the notch, such as would be the case with the fissures resulting from intercrystalline corrosion, the more pronounced the effect would be. The shortened life of such parts which in service are subjected largely to vibratory or repeated stresses is to be expected and should cause no surprise.

Practical Aspects of Intercrystalline Embrittlement.

Certain chemicals, such as calcium chloride solutions, used as "anti-freeze" in the water-recovery systems of an airship may very promptly cause intercrystalline embrittlement of duralumin, thus rendering a duralumin girder upon which it may be spilled, quite unsafe. Even when no active corrodent is in evidence, as in planes operating solely inland, brittleness may develop after long service. In fact, sheet duralumin kept in a drawer of an office desk (Bureau of Standards) has been found to be embrittled as proved by endurance tests and by microscopic examination. Varnishing the surface of the material cannot be depended upon as a protection against this form of corrosion attack; evidence of well-advanced deterioration has been found in *See also: R. R. Moore, "Effect of Corrosion upon the Fatigue Resistance of Thin Duralumin," American Society Testing Materials, Proc. 27, Part 2, 128, 1927.

varnished sheet duralumin.

On the other hand, a great deal of the duralumin sheet examined after long service under rather corrosive conditions has not been found to be harmed, that is, in an intercrystalline manner, by time, exposure, or use. In fact, the existence of any pronounced tendency of this material toward embrittlement was initially questioned by makers of duralumin and by both makers and users of aircraft. When their attention was called to it and they looked for it. however, they all found it and it has been met in duralumin of foreign as well as American manufacture.* Many of the early observations made at the Bureau of Standards on embrittled sheet duralumin were on material of German manufacture (Fig. 2). The possible shortcomings of sheet duralumin in this respect are now realized and admitted by the manufacturers of the alloy and in the investigation on this subject, forming the basis of the succeeding reports of this series, the leading American manufacturers have cooperated in a very commendable way.

The fact that most duralumin parts of aircraft have lasted *See, for example: C. F. Jenkin's "Note on the Possible Gradual Deterioration of Duralumin," Appendix II of "Report of the Airworthiness of Airship Panel," British Aeronautical Research Committee Reports and Memoranda No. 970, 1924.

R. R. Moore, "Discussion of Fatigue Testing," Proc. Am. Soc. Test. Materials 27, Pt. 2, p.152, 1927.

Tord Angström, "Influence of Salt Water on Duralumin," L'Aeronautique, 7, p.77, 1925.

well indicates that the difficulty is by no means insuperable, once the cause is known. It can be positively stated that the embrittlement results from sources outside the duralumin and that it is not a spontaneous disintegration of the metal itself. If the material is made more resistant to corrosion of this type or if the corroding agents are kept out of contact with the material, no deterioration will ensue.

The danger from embrittlement decreases as the cross section of the duralumin increases. Thick-walled tubing has been found practically unharmed after exposure which has quite ruined thin sheet on the same airplane. There seems to be no important embrittlement problem in the case of propellers, for example. On the other hand, unprotected thin sheet (of 0.008" thickness) may be gravely injured by a few days' exposure to air and distilled water, or by a few weeks' exposure to the weather inland.

The insiduous nature of the type of corrosion which causes embrittlement below the surface without necessarily being accompanied by visible corrosion on the surface, and the failure of ordinary coatings to afford complete protection against the attack, makes it essential that the cause be located and the attack prevented instead of relying upon inspection, removal and replacement of affected material.

There is no satisfactory substitute for duralumin. It stands to-day as an essential material for sircraft. Unless its reliability and permanence can be assured, aircraft development

will be hampered. It has been the purpose of the investigation reported in this series of technical notes to develop methods of improvement and of protection which would assure the reliability and permanence of duralumin.

Just as there was a lag between the first finding of the phenomenon of intercrystalline embrittlement and a general understanding of its importance, so is there now a lag between the development of satisfactory methods of avoiding embrittlement and their widespread application. The first stage was one of false security, the second (and present) one of unnecessary fear, and the third will be one of real security.

As has already been pointed out,* it is now no longer a question whether or not the intercrystalline attack can be prevented, but merely which one of several effective methods should be chosen in a particular case.

Hence, this series of reports should tend to emphasize the dependability of properly treated and protected duralumin as a material for aircraft construction.

Bureau of Standards,

January 25, 1928.

^{*}Thirteenth Annual Report of the National Advisory Committee for Aeronautics, 1927, p. 45.

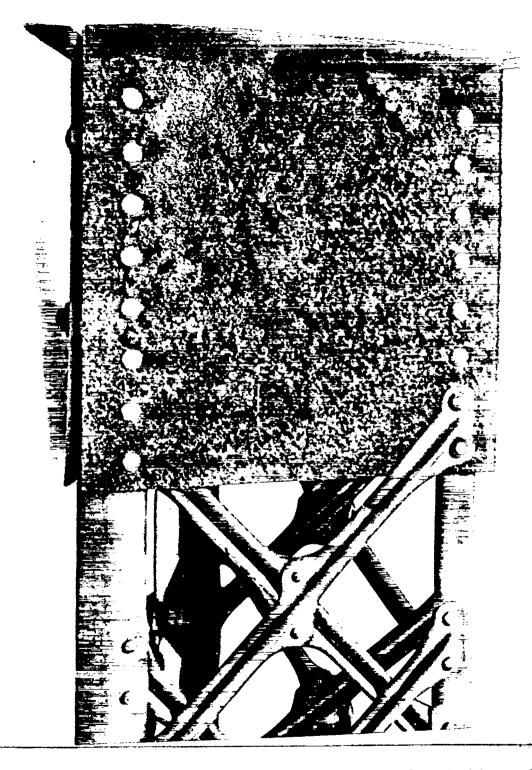


Fig.1 Part of a duralumin girder of the type used for airships, after 3 years exposure to the atmosphere. The steel end plates are badly rusted while the duralumin channels and lattices show no appreciable surface attack.

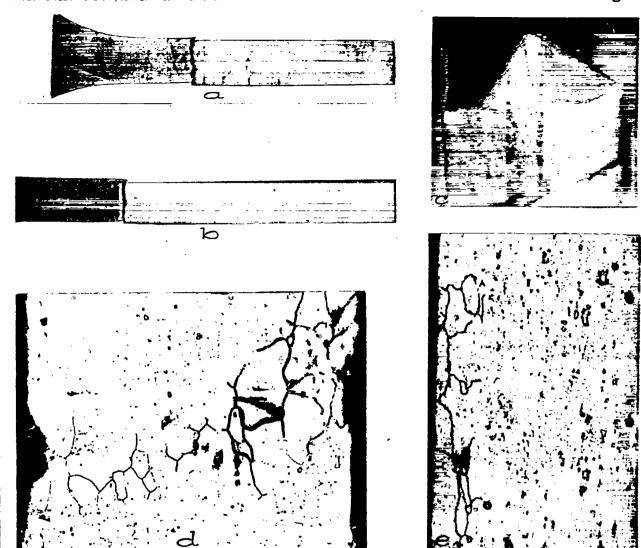


Fig. 2 Effect of intercrystalline corrosion on the mechanical properties of sheet duralumin.

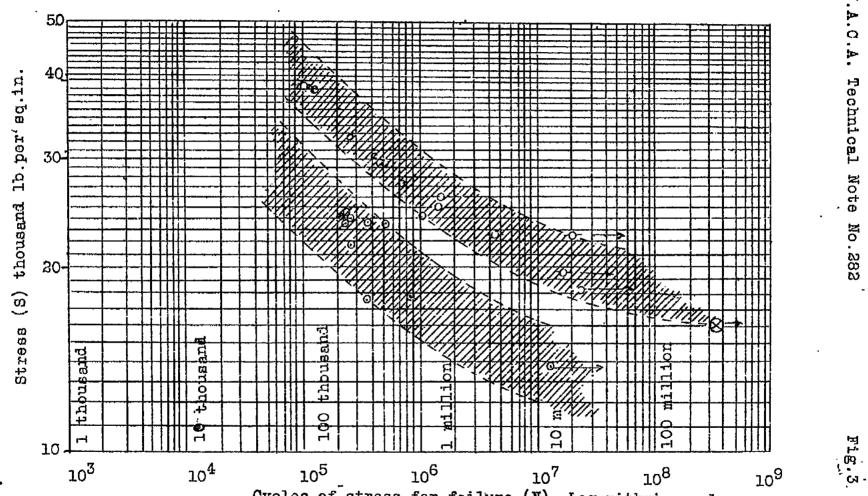
- a. Varnished sheet (.057") exposed to the weather 8 months, x 2; ultimate tensile strength 48,600 lb./in.², elongation (2 inch) 6.5%
- b, Another sheet (.048") after 1 year in storage, x 2; ultimate tensile strength, 55,000 lb./in.², elongation (2 inch) 16 per cent. Specified values for a and b, 55,000 ultimate tensile strength; 30,000 lb./in.² 'yield' point; 18 per cent elongation.
- c. Sheet material (.012") used as wing covering on J-L airplane exposed 2 years to the sea air, severely bent to show the degree of embrittlement, $x 2\frac{1}{2}$.
- d, Cross section of the material of c, x 250.
- e. Cross section of a sheet of duralumin which was kept indoors (in an office desk) for several years, x 500.

o Longitudinal Transverse • Forgoing, 1" diameter (approx.) .ote. An arrow signi-

o Embrittled material

e Templin, A.S.T.M. proc. 27, p. 140, 1927.
Determined on 1/4" round spec. from 1" round.

Note. An arrow signifies a specimen removed unbroken.



Cycles of stress for failure (N). Logarithmic scale. Fig. 3 Results of flexural fatigue test of sheet duralumin, approx.040 thick. The stress range indicated for the failure of the embrittled specimens applies only to the set of specimens used, for different lots of embrittled material it may vary very considerably according to the severity of the corrosive attack.